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FLUORINE GAS AS A CLEANING AGENT FOR APOLLO BULK-SAMPLE CONTAINERS

R. H. Liddle J. M. McIntyre C. E. McAlister

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ABSTRACT

A technique has been developed for cleaning Apollo bulk-sample containers using fluorine gas as the cleaning agent.

CONTENTS

SUMMARY	5
INTRODUCTION	6
CLEANING APOLLO BULK-SAMPLE CONTAINERS	7
Bulk-Sample Collection Bag	7
Apollo-14-Style Bulk-Sample Container	
Apollo-15-Style Bulk-Sample Container	8
Cleaning Requirements	12
Fluorination Procedures and Facilities	15
Applicability of Fluorination	15
Fluorination for Biological Sterilization	
CONCLUSIONS	21
A CKNOWLEDGEMENTS	วว

SUMMARY

To provide better sample return containers for the Apollo program, a new type of bulk sample bag was designed and fabricated, at the Oak Ridge Y-12 Plant, (a) from a Teflon laminate. This particular material required a new cleaning technique to provide the needed cleanliness levels. Using careful handling techniques and modern clean-room facilities, surface contamination levels of 50 nanograms per square centimeter were attained routinely by fluorine gas treatment. These levels of cleanliness were certified using nonvolatile residue techniques supported by gas chromatographic data.

Biological sterilization studies show that fluorine gas, even at low concentrations, is an effective sterilant. Compatibility studies of the gas with various metals show that fluorine is compatible with many common metals in the concentration levels required for effective biological sterilization. Thus, fluorine gas is shown to be an important and flexible contamination-control medium.

⁽a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

INTRODUCTION

The prime requirement for the design and fabrication of all sampling hardware for the Apollo missions is that the scientific integrity of the lunar samples be preserved in order that the principal investigators might make a true appraisal of the lunar surface. Thus, the sampling equipment must be free of terrestrial contamination to the extent that their presence will not interfere with the parts-per-billion (nanogram) analyses of the lunar samples. The purpose of this report is to describe a technique developed at the Y-12 Plant for cleaning Apollo bulk-sample containers using fluorine gas as the cleaning agent.

CLEANING APOLLO BULK-SAMPLE CONTAINERS

BULK-SAMPLE COLLECTION BAG

Apollo-14-Style Bulk-Sample Container

Weigh bags used on Apollo missions prior to Apollo 14 were constructed from 5-mil-thick Teflon film (Figure 1) with aluminum rims sealed into the top and bottom. This

arrangement produced a 4 x 8 x 16-inch container when opened. These containers were uniquely designed to be hung on the Apollo Lunar Spring Scale or on the astronauts' suits during the extra-vehicular activity. Closure of this type of bag was accomplished by flattening the square aluminum ring at the top, rolling it down the bag approximately three times, and bending it into a "Z" shape to prevent unrolling. Although seemingly adequate, actual use revealed several faults in this first style of weigh bag, namely: the 5-mil film construction provided little resistance to puncture by sharp rocks; and, further, its inability to retain its shape after loading made closing of the Apollo Lunar Sample Return Container (ALSRC) difficult. Also, a better closing system was needed to provide for the required segregation of the samples.

As a result of some engineering modifications subsequent to Apollo 13, the Apollo-14-style weigh bag was designed (Figure 2). This bag is constructed from a laminate consisting of one sheet of 3-mil FEP Teflon vulcanized to one ply of TFE Teflon cloth. (This material has the



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Figure 1. TEFLON FILM WEIGH BAG.

consistency of light oilcloth.) A folding top band of stainless steel that is 3/8 inch wide by 1/16 inch thick forms a 6 1/2 by 8-inch opening. A bottom band of 1/8-inch aluminum wire forms the lower section of the bag, and a 4-ply Teflon handling strap is provided around the front of the top side. The design of this style of weigh bag makes use of a purse-type top closure and may be hung from a tether hook, the spring scales, or on the Modular Equipment Transport while on the lunar surface. The bag must be stowed either on the Modular Equipment Storage Area or in the ALSRC during the translunar portion of the mission. The filled bags may be stowed in the Lunar Module, the Command Module, or in the ALSRC during the transearth portion of the Apollo mission. Double-stitched lines are placed on the bag at distances of seven and eleven inches from the bottom. The lower fill line is used for a filling reference by the astronaut when the filled bags are to be stored in pairs in the ALSRC. The fill line at the eleven-inch level is a volumetric reference for other storage configurations. When supported from the astronaut's suit, this type of bag can be readily opened by pulling out on the handle or closed by pressing the palm of the hand against the front of the bag in a horizontal motion. When a more positive type of closure is



Figure 2. APOLLO-14-STYLE WEIGH BAG.

required, as for inbound storage, the thumb and forefinger of one or both hands can be pressed firmly on the top corners of the closed hardware to snap past the double stitching between the hardware.

Availability of Teflon materials was limited to film and woven cloth, neither of which provided the flexibility or puncture resistance needed for the new type of weigh bag. It was decided that an effective laminate of the two materials could be used.

Permanent lamination is achieved by pressing a sheet of 3-mil film and a layer of woven fabric between heated stainless steel platens at 250 psi and 277° C for one-half hour, after which the platens are cooled and the laminate removed. (The platen-press apparatus can be seen in Figure 3.)

Because of the extremely high degree of cleanliness required prior to using the finished bags, the amount of contamination "bonded in" or introduced to the bonded material during this operation must be kept at an absolute minimum. To this end, the as-received materials are given an ultrasonic

rinse with Precision Cleaning Agent (PCA)-grade trichlorotrifluoroethane to remove the initial contamination. The materials, received in large rolls, are then cut to the desired size and placed in a Class 100, horizontal-flow clean bench to prevent the introduction of body-generated contaminants (Figure 4). Finally, the loaded platens are bagged in clean polyethylene and transported to the press area. To limit the introduction of contamination during the pressing operation and subsequent removal of the finished material, the press apparatus is equipped with an air supply system and a High-Efficiency Particular Air (HEPA) filter behind the platens. This system provides a constant stream of HEPA filtered air across the platen area in the direction of the operator.

Following lamination, the material is sealed in clean polyethylene bags and sent to the appropriate contractor for sewing with Teflon thread according to the design specifications. This sewing operation takes place in a Class 10,000 clean area.

Apollo-15-Style Bulk-Sample Collection Bag

Preflight equipment evaluation by the Apollo 15 crew resulted in a request that the bulk sample collection bag be of a size to match the interior size of the ALSRC, so that all sampling equipment could be packed in the bag, within the ALSRC, for the translunar

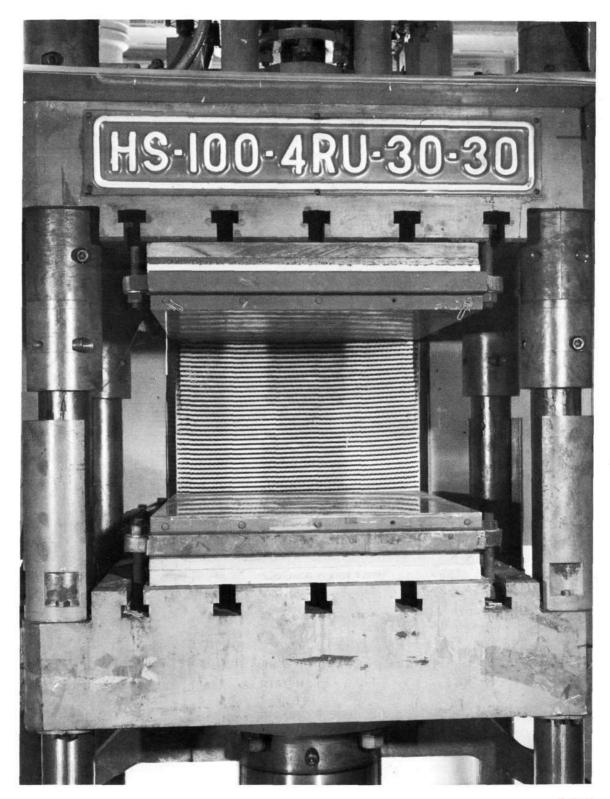


Figure 3. PLATEN-PRESS APPARATUS FOR LAMINATING TEFLON.



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Figure 4. CUTTING TEFLON CLOTH ON A CLASS 100 HORIZONTAL-FLOW CLEAN BENCH.

portion of the mission and that all samples could be packed in the same manner for the transearth portion. In addition, two types of bags were requested, due to changes in the sample weight limits for lunar module liftoff. One style was designed to be packed in the ALSRC and to provide segregation of the sampling hardware to prevent damage. The other style was designed for use in returning various extra samples outside of the ALSRC. Because of the increased size and load weight, a heavier material was needed to meet the requirements of puncture resistance and size retention.

The results of these changes are the Type 1 and Type 2 Sample Collection Bags (SCB's) seen in Figures 5 and 6, respectively.

These sample collection bags are constructed of one ply of TFE Teflon cloth vulcanized between two sheets of FEP Teflon film. The vulcanized material has the consistency of heavy oilcloth. A rectangular band of stainless steel, 3/8 inch wide by 1/16 inch thick, forms a 6 5/8-inch by 8 3/4-inch opening. Two Teflon 4-ply straps are provided on the front side near the top and bottom to facilitate handling. Exterior restraint points have been provided on the rear of the bags of both types. The top attachment point (restraint bracket) consists of a formed band of 1/32-inch-thick by 3/8-inch-wide stainless steel, pop riveted to a stainless steel band inside of the bag in four places. This restraint bracket provides the

vertical support of the SCB on the Apollo Lunar Hand Tool Container (ALHTC) or the Lunar Rover Vehicle (LRV). A two-ply Teflon cloth strap, one inch wide, is the lower restraint, and is used to prevent excessive horizontal motion of the bag after attachment to either of these units. The SCB's have a full-opening flip-type cover for the easy loading of bulk samples. The Type-1 SCB is free of internal and external pockets since it will be used as the extra-sample unit; the Type-2 bag has three interior pockets for the core tubes along the inner left side facing the front of the bag. In addition to the inner pockets, two exterior pockets are provided on the front panel of the Type-2 bags to retain one Magnetic Shield Sample Container (MSSC). These exterior pockets conform to the basic envelope size of the SESC and MSSC with



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Figure 6. TYPE-2 SAMPLE COLLECTION BAG.

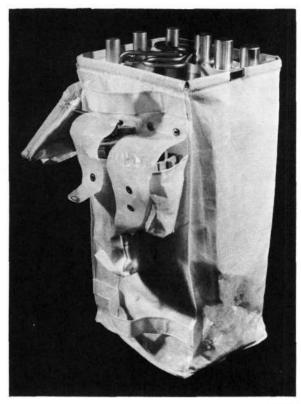


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Figure 5. TYPE-1 SAMPLE COLLECTION BAG.

allowances made for grasping the containers for removal. Figure 7 shows a Type-2 SCB with pockets loaded. The inside surface of the top cover and the bottom of the bag have a full coverage with a 1/8-inch, 7-ply aluminum wire mesh pad to prevent the ends of the core tubes from damaging the top cover and bottom of the SCB if struck by a firm object.

The SCB can be removed from the ALSRC, ALHTC, or LRV by using the strap handle near the top of the bag; however, when installing the SCB on the ALHTC or the LRC, both strap handles on the front of the bag are used. The top cover latch is operated by springing the SCB top cover rim out approximately 3/16 inch. The SCB



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Figure 7. TYPE-2 SAMPLE COLLECTION BAG WITH LOADED POCKETS.

is opened or closed by pulling the Teflon latch loop firmly out from the side of the bag with a rotating motion. The catch will latch automatically if the cover is firmly in place when the loop is released.

Once again a satisfactory material for the construction of these new bags had to be developed. After further study it was shown that another sheet of 3-mil Teflon film could be laminated to the material for the Apollo-14-style bag, essentially sandwiching the woven fabric between two sheets of film, and providing the required puncture resistance and size-retention characteristics. This new material is prepared for pressing in the same manner described for the Apollo-14-style material using the same clean facilities and careful handling techniques. Permanent lamination, with no void areas, is achieved by pressing the materials between two platens at 335 psi and 310° C for one-half hour, after which the platens are cooled and the laminate removed.

CLEANING REQUIREMENTS

To achieve overall cleanliness, the bulk sample collection bags used prior to Apollo 14 were subjected to rigorous solvent cleaning techniques. (b)

The method of cleanliness certification used for all of the Apollo sampling hardware, including the new-style weigh bags, involved a combination of nonvolatile residue measurements and gas chromatographic analyses. The last step in the final cleaning procedure involved immersion in a certification bath and subsequent agitation. A one-gallon sample of the certification mixture was collected before and after immersion of the hardware. These samples were then evaporated at 100° F under a reduced pressure until the residue weights were constant. The residue from each sample was then weighed. Knowing the solvent-to-surface area ratio of the certification bath, and assuming that the change in the nonvolatile residue weight after immersion of the hardware was due to hardware contamination, it was possible to calculate the residual contamination on the hardware surface from the difference between the two residue weights. These residues were then

⁽b) R. H. Liddle, J. C. Little, J. M. McIntyre, and F. D. Mundt; *Heating, Piping, and Air Conditioning*, 42, p 67 (1970).

redissolved in two cubic centimeters of nanograde benzene, and a ten-microliter sample of these solutions was injected into a gas chromatograph programmed between 100 and 250°C. Using a blank of decane treated in the same manner and the assumption used before, the areas under the two sample curves could be used to calculate the residual contamination. It should be noted that these methods of certification are used primarily because of their similarity to the methods used for the analyses of the lunar material for organics.

The TFE-woven Teflon cloth used in the fabrication of the new style weigh bags is available from the manufacturer in two forms: "natural" and "bleached". The natural fabric is brown in color and is the direct product of their manufacturing process; the "bleached" fabric is white in color resulting from a bleaching step with 95 percent sulfuric acid and 5 percent nitric acid at approximately 600° F. The TFE Teflon thread used in sewing the bags is only available in the natural form. Attempts to certify the required cleanliness level after the cleaning sequences just outlined for the older-style weigh bags either failed or were much too close to the allowable maximum. For this reason, steps were taken to isolate the inherent contamination in the Teflon fabric and thread used.

Gravimetric analyses of "natural" Teflon fabric and thread by leaching with a 95 percent sulfuric acid-5 percent nitric acid mixture at 600° F for one hour showed a total of 3.8 percent non-Teflon components. Infrared spectrophotometric analyses of the materials leached from the fabric and thread samples with water, trichlorotrifluoroethane, acetone, and benzene showed cellulose, carbon, and polyethylene oxide paraoctylphenol condensate as the major constituents.

Gravimetric analyses of the "bleached" fabric by the same method previously outlined, revealed that the same non-Teflon components were present, but only in quantities of 0.5 to 1.0 percent.

Manufacturer and supplier representatives were contacted and they indicated that the introduction of these impurities is basic to their operations. Based on this information it was decided that: (1) the bleached fabric would be used for fabrication, and (2) some type of cleaning method would have to be developed for the contaminants inherent to the bleached cloth and the natural thread.

Further study also revealed that a new cleaning technique was needed to remove entrapped lint particles which were bonded into the laminant in spite of the precautions taken to prevent it. These "bonded in" particles could not be removed by the ultrasonic solvent cleaning methods ordinarily used, but their presence could nonetheless contaminate the other pieces of hardware during the vacuum conditions of the lunar mission.

The first, and obvious, method attempted involved further "bleaching" by the hot-acid method used by the manufacturer. This method caused severe wrinkling and strength loss of the laminated material and did not remove the entrapped lint particles.

Several step-wise fluorination procedures were tried, and one, which will be described later, was found to be successful in removing all detectable non-Teflon impurities. This process produced a white material which, when leached in water, trichlorotrifluoroethane, acetone, and benzene, showed no impurities by infrared spectrophotometric analyses. Thread

strength was only reduced slightly. (Break-strength tests of the thread revealed a break strength of 5.9 pounds after fluorination as opposed to 6.6 pounds before.) Materials to be fluorinated were: (1) given an ultrasonic rinse in PCA-grade trichlorotrifluoroethane to remove gross amounts of organic contaminants; (2) dried at aspirator vacuum and at 300° F for one hour to remove all traces of the trichlorotrifluoroethane; (3) sealed in a precleaned Teflon bag to prevent the introduction of contamination prior to being placed in the fluorination chamber. Once in the fluorination room, the bags were opened at each end to permit fluorine gas flow, and the components were placed in the fluorination chamber.

The following step-wise fluorination procedure was found to be sufficiently slow to prevent "burning" the material, and yet adequate to produce the cleanliness levels described previously:

- Evacuate the chamber by means of an air aspirator, and backfill with a mixture of 95
 percent nitrogen and 5 percent fluorine. Hold the system at room temperature for two
 hours.
- Evacuate the chamber and backfill with 90 percent nitrogen and 10 percent fluorine, and hold at room temperature for two hours.
- 3. Evacuate the chamber, backfill with a mixture of 80 percent nitrogen and 20 percent fluorine, and hold at room temperature for two hours.
- 4. Evacuate the chamber, backfill with 50 percent each of nitrogen and fluorine, and hold at room temperature for one hour.
- 5. Evacuate and backfill with 50 percent each of nitrogen and fluorine, heat to 300° F, allow the system to cool to room temperature, and hold at room temperature for one hour.

Following this procedure, the system was cooled, purged with nitrogen, and opened. The bags were immediately sealed for transportation to the post-fluorination handling and final cleaning area.

The texture of the laminated fabric was not changed by the fluorination operation, and all visible indications of the entrapped lint were removed.

Teflon fabric weigh bags fluorinated by this method were cleaned by the precleaning method, outlined previously, prior to any further solvent cleaning. Results indicated a detectable contamination of 50 nanograms per square centimeter of surface area. Examination of the residual contaminants indicated that approximately 20 percent were water-soluble fluorides.

Fluorinated weigh bags were cleaned by the standard final cleaning method, and certification revealed a residual contamination level of well below the required limit of ten nanograms per square centimeter, indicating that there is no need for preliminary cleaning after fluorination. In fact, contamination levels for other types of components, after the standard precleaning operation, were routinely 100 nanograms per square centimeter of surface, which is much greater than that for the weigh bags after fluorination.

This fluorination method of precleaning is also much more economical in terms of manhours required and material cost than the previous solvent method.

FLUORINATION PROCEDURES AND FACILITIES

Development of a step-wise fluorination procedure was the key to the success of using fluorine gas for cleaning. The intense heat produced when fluorine gas reacted with organic impurities in the Teflon fabric caused the first materials treated to be essentially destroyed. For this reason, a fluorination procedure was developed to provide for slow fluorination of the material, and yet to produce the desired cleanliness level.

The fluorination operation was performed at the Oak Ridge Gaseous Diffusion Plant in a laboratory especially equipped for handling fluorine gas.

The fluorination area is equipped with several chambers of the type used for the ALSRC fluorination activities. The actual chamber used is shown in Figure 8. It is basically a resistance-heated tube furnace, with all internal parts constructed from fluorine-resistant Monel. The furnace door is also of Monel, and is closed by means of a "spinder" arrangement with a gas-tight seal effected by a fluorosilicone O ring. Materials to be fluorinated are placed in a perforated Monel rack, as indicated in Figure 8. The furnace is equipped with resistance heaters capable of reaching 600° F, a filtered nitrogen supply, a nitrogen aspirator system, temperature control equipment, and a fluorine gas supply. For safety purposes, the fluorine gas (received in high-pressure cylinders) is first expanded into a large ballast tank or "pig" where the pressure is reduced to 5 psi. The fluorine gas removed from the chamber by the nitrogen aspirator is passed through a standard caustic scrubber system prior to being exhausted to the atmosphere.

Even though the fluorination operation provides a high level of cleanliness, a further solvent cleaning is necessary to attain the desired cleanliness level of less than ten nanograms per square centimeter. The final cleaning operation outlined previously is used with one minor change. Because it was found that a large percentage of the contaminants remaining after fluorination are water soluble, and since Teflon does not "wet" in pure water, nanograde isopropyl alcohol is added in a ratio of 1 to 10 to the first water bath. With this modification, the Teflon fabric components are routinely cleaned to well within the required certification level.

The post-fluorination handling and final cleaning were performed in a Class 100 VLF clean room. The layout of the clean room is seen in Figures 9 and 10.

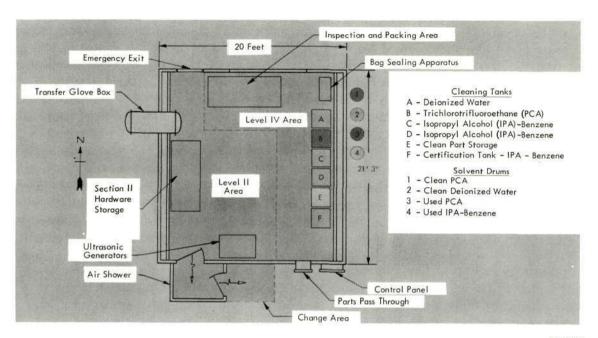
APPLICABILITY OF FLUORINATION

To determine the flexibility of the fluorination procedure, a number of metals and alloys were submitted to various steps of fluorination cleaning to determine their compatability with the procedure. Specimens (1" x 1" x 1/8") of tantalum; Inconel; Types 301, 302, 304-L, and 17-7 pH stainless steel; and Types 1100-H14, 5052, and 2024 aluminum alloys were investigated. The specimens were precleaned to remove excessive organic contaminants by washing them in ultrasonically at itated PCA-grade trichlorotrifluoroethane at room temperature for 20 minutes. The specimens were then individually packaged in Teflon film bags.



Figure 8. FLUORINATION CLEANING CHAMBER.

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Figure 9. LEVEL-IV CLEANING LABORATORY.

Three sets of these metals and alloys were submitted to the various steps in the fluorination cleaning procedure. The first set was exposed to a gas mixture of 5 volume percent fluorine-95 volume percent nitrogen at one atmosphere pressure and room temperature for 30 minutes. The tantalum specimen was tarnished, but there was no sign of attack on the

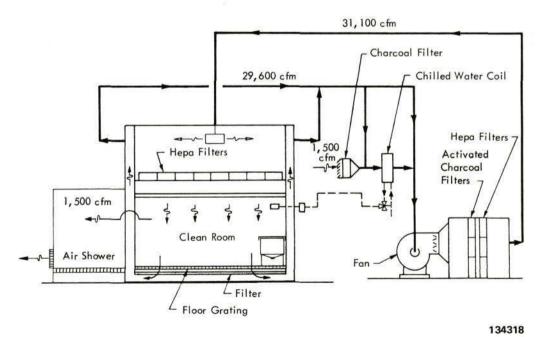
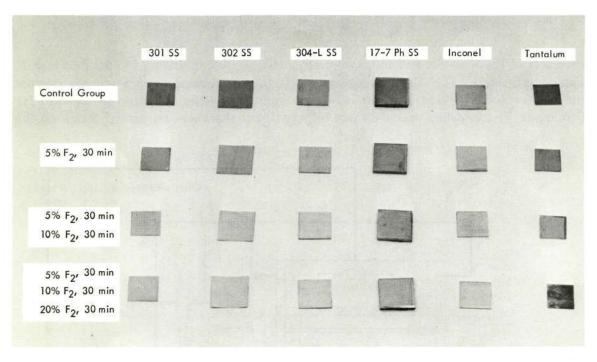


Figure 10. MECHANICAL EQUIPMENT AND AIR FLOW IN THE LEVEL-IV CLEANING LABORATORY.

other specimens. A second set was exposed to the same gas mixture at one atmosphere pressure and room temperature for 30 minutes, followed by a second exposure to a gas mixture of 10 volume percent fluorine-90 volume percent nitrogen at one atmosphere pressure and room temperature for 30 minutes. Corrosive attack of various areas of the tantalum specimen was noted, but the other specimens showed no attack. The third set was exposed to a three-step procedure: (1) a gas mixture of 5 volume percent fluorine-95 volume percent nitrogen at one atmosphere and room temperature for 30 minutes; (2) a gas mixture of 10 volume percent fluorine-90 volume percent nitrogen at one atmosphere and room temperature for 30 minutes; (3) a gas mixture of 20 volume percent fluorine-80 volume percent nitrogen at one atmosphere and room temperature for 30 minutes. The tantalum specimen showed general surface roughness due to fluorine attack, but the other specimens showed no sign of corrosion. Figure 11 gives a view of a number of the specimens used in these tests. No detectable organic residue could be leached from the specimens after the third fluorination step. This leach consisted of immersing the specimens and ultrasonically agitating them in nanograde benzene for 30 minutes. The solvents were evaporated and the nonvolatile residues weighed. Gas chromatographic analyses were also used. The contamination was less than 50 nanograms of nonvolatile organic residue per square centimeter of surface area.



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Figure 11. METAL SPECIMENS THAT WERE EXPOSED TO THE FLUOR INATION CLEANING PROCEDURE.

These studies indicate that the proposed fluorination cleaning procedure can also be used effectively for cleaning many types of metals and alloys. However, materials, such as tantalum and glass, which are susceptible to fluorine attack should not be considered for fluorination cleaning.

FLUORINATION FOR BIOLOGICAL STERILIZATION

Since fluorine gas is an excellent oxidizer, it was apparent that the fluorination cleaning procedure developed for the Apollo bulk-sample containers could also be an effective sterilization procedure for biological specimens. Investigations were conducted to determine the effectiveness of each step of the fluorination procedure for sterilization.

Type 1100-H14 aluminum wire mesh wrapped into cylinders about one-half inch in diameter and two inches long was used as a support for a bacterial contaminant. Thirty of the wire-mesh samples were sterilized by conventional techniques using a steam autoclave. Ten samples were used as sterile controls and twenty samples were contaminated with a highly resistant strain of spore-forming bacteria called Bacillus Globiggii. A bacteria count showed between 10^7 and 10^8 spores per sample. Five sterile samples and five contaminated samples were held in the Class 100 VLF clean room for about one week to determine the ability of the clean room to maintain sterile conditions. After one week another bacteria spore count indicated that the sterile samples remained sterile and the contaminated samples were not contaminated by foreign bacteria. The remaining five sterile samples were placed in clean fluorinated Teflon film bags and sealed. They were then transferred to the fluorination furnace and opened immediately before placing them inside. Finally, the samples were subjected to the fluorination cleaning procedure previously described in this report. Upon opening the chamber, the bags were resealed and the samples transferred to another bacteria-free area where a bacteria count was conducted. No contamination could be found on the sterile samples. These studies indicate that sterile matter can be handled in the Class 100 VLF clean room for extended times and can also be transferred to and from a fluorination chamber without being contaminated by bacteria.

The remaining fifteen contaminated samples were subjected to various steps of the fluorination cleaning procedure. These specimens were transferred to and from the fluorination chamber in sealed, sterile Teflon film bags. Five were exposed to a gas mixture of 5 volume percent fluorine-95 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes. The spore count dropped from the original 10^7 - 10^8 spores per sample to 10^5 - 10^6 spores per sample after fluroination, or a 99 percent kill.

A second group of five samples was exposed to a mixture of 5 volume percent fluorine-95 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes, followed by an exposure to 10 volume percent fluorine-90 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes. The spore count per sample after this fluorination step dropped to 10^4 - 10^5 spores, or a kill of 99.9 percent.

A third group of five samples was exposed to a mixture of 5 volume percent fluorine-95 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes, then a mixture of 10 volume percent fluorine-90 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes, and finally to a mixture of 20 volume percent fluorine-80 volume percent nitrogen at atmospheric pressure and room temperature for 30 minutes. The spore count after this procedure was approximately 10³ spores per sample, or a kill of about 99.99 percent.

The effectiveness of sterilization by fluorination was well demonstrated by these investigations. It is apparent that the procedure for fluorination cleaning was not 100 percent effective in sterilizing against highly resistant spore contamination, but the procedure could be optimized in order to obtain a 100 percent kill. Longer exposure times, higher concentrations of fluorine, and/or a slightly elevated temperature should be considered in optimizing the procedure.

CONCLUSIONS

Precision cleaning to a level of less than ten nanograms of organic contaminants per square centimeter of Teflon fabric and Teflon film-fabric laminates is being routinely attained using fluorine gas in conjunction with precision cleaning operations using ultrapure solvents. A Class 100 VLF clean room that employs a double HEPA filtration system and an activated-carbon filtration system is used to maintain cleanliness prior to subsequent operations.

The fluorine gas cleaning process was effective in cleaning organic materials from a number of fluorine-resistant metals such as the stainless steels and certain aluminum alloys. This discovery may prove to be very beneficial to the electronics and other industries that must handle ultrapure components in order to assure a quality product. Fluorine gas was also effective in sterilizing metal surfaces and may prove to be excellent for decontaminating such items as surgical instruments. Teflon gauze sterilized in this manner may be beneficial to surgical techniques.

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